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MEASUREMENT OF THE CONCENTRATION OF OXYGEN ATOMS  
IN FLAMES BY THE USE OF NO

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and  
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- USSR -

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MEASUREMENT OF THE CONCENTRATION OF OXYGEN ATOMS  
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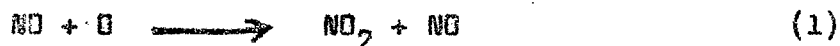
-USSR-

[Following is a translation of an article "Izmereniye kontsentratsii atomov kisloroda v plamenakh pri pomo-shchi NO" (English version above) by L. V. Karmilova and V. N. Kondrat'yev in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol XXV, No 3, Mos-cow, 1951, pp 312-322.]

Oxygen atoms undoubtedly belong to the number of basic ac-tive centers entering into the chain mechanism of combustion re-actions. Therefore, the observation of oxygen atoms, and meas-urement of their concentration in flames, is one of the most im-portant problems in the investigation of the chemistry of flames and combustion theory. A few years ago, one of the authors pro-posed as a solution to this problem a method (1, 2) based on measurement of the absolute output of light related to the so-called flame spectrum of CO. However, this method cannot be con-sidered promising until the mechanism of excitation of the indi-cated spectrum--which proved to belong to the molecule of O<sub>2</sub> (4) in the discrete zone section (and not CO<sub>2</sub> as was assumed earli-er)--has been established.

For this reason, along with the method mentioned, all other methods are of great interest that make possible the solution of the same problem of identification and measurement of the oxygen atom concentration in the combustion zone by independent means.

Gaydon (3) has proposed another spectroscopic method based on the observation of the characteristic yellow-green light aris-ing upon the presence of nitrogen oxides and atomic oxygen in the flame, related to the process



This process is the reverse of the process of predissociation of  $\text{NO}_2$  which takes place in the region  $\lambda \approx 4000 \text{ \AA}$ .

Gaydon uses his method in a purely qualitative fashion. The possibility of applying it as a quantitative method proved to be the main task of the present investigation.

#### THEORY OF THE METHOD

Although emission of yellow-green light of  $\text{NO}_2$  is also related to a recombination process (1), in order to calculate the intensity of this light we do not need to use the method of de-

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[TEXT CONTINUED ON PAGE 3]

termining the effective magnitude of recombination accompanied by emission of light, which was used by V. N. Kondrat'ev and A. I. Leypunskiy (5) in the case of processes of the type  $X+X' = X_2 + hv$  (X is a halogen atom, X' is an excited X atom), based upon the principle of microscopic (detailed) equilibrium. Actually, on the basis of the latter value, recombination (as has been demonstrated by A. N. Terenin and N. A. Prilezhayev) may be related to the coefficient of absorption (6), being a measure of the probability of the reverse process. The latter, however, is accurate only in the case of ordinary photodissociation and does not take place in the case of predissociation where the coefficient of absorption determines the total probability of absorption; that is, the sum of probabilities of excitation and photodissociation.

This is graphically made clear in Fig. 1, in which the function is shown for  $k$ , the absorption coefficient of  $NO_2$  (determined as  $k = \frac{1}{l} \ln \frac{I_0}{I}$ ,  $p$  in mm Hg,  $l$  in cm) with respect to the wave length  $\lambda$  in  $m\mu$  (according to the measurement data of Dickinson and Baxter (7)--small circles, and Holmes and Daniels (8)--small crosses) and the function of quantum yield  $\eta$  during photochemical decomposition of  $NO_2$  (according to the data of Norrish (9)-- $\nabla$  and Holmes and Daniels (8)-- $\Delta$ ).

In Figure 1 also, the dotted curve represents a sample (in view of the absence of quantitative data) function of the brightness of fluorescence of  $NO_2$  upon excitation by various wave lengths (9). It is apparent from the drawing that at similar absorption coefficients in spectral regions close to  $\lambda = 436 m\mu$  and close to  $\lambda = 366 m\mu$  excitation of the molecules of  $NO_2$  ( $\eta = 0$ ) takes place in the first region, and photodissociation in the second (absence of fluorescence).

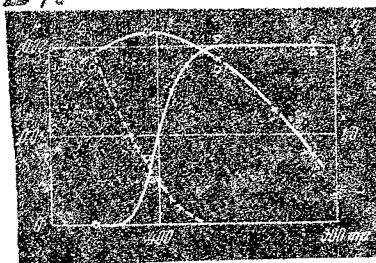
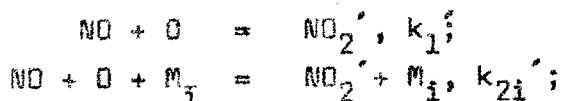
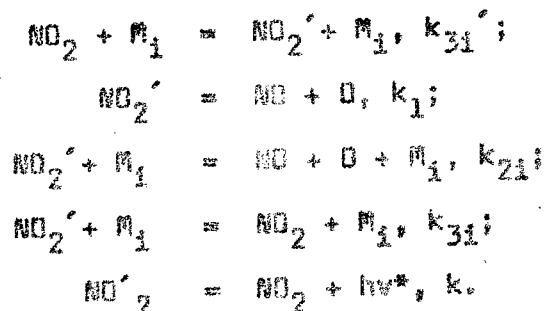


Fig. 1

Since the coefficient of absorption of  $NO_2$  could not be used for calculation of the magnitudes of recombination of NO and O, we settled upon the following method for calculating the intensity of the yellow-green light in flame conditions.

Under these conditions it is necessary to take into account the following elementary processes taking place among O, NO, and  $NO_2$ :



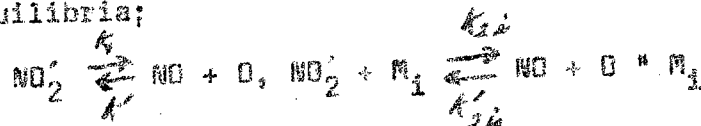


Here,  $k_1'$ ,  $k_{21}'$ , etc., are rate constants,  $\text{M}_i$  is a particle of the  $i$ -th sort. Determining from the stationary condition  $\frac{d(\text{NO}_2')}{dt} = 0$ , the stationary concentration of the excited molecules of  $\text{NO}_2$ , we will obtain for the intensity of emission per unit volume of flame I

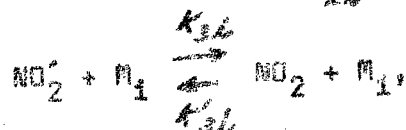
$$I = k(\text{NO}_2') = k \frac{[k_1' + \sum k_{21}'(\text{M}_i)] (\text{NO}) (\text{O}) + \sum k_{31}'(\text{M}_i)(\text{NO}_2)}{k + k_1 + \sum k_{21}(\text{M}_i) + \sum k_{31}(\text{M}_i)} h\nu^*. \quad (2)$$

Here,  $h\nu^*$  designates the quantity of the emitted quanta.

The constants  $k_1'$ ,  $k_{21}'$ , and  $k_{31}'$  may be expressed, on the basis of the principle of detailed equilibrium, by the constants  $k_1$ ,  $k_{21}$ , and  $k_{31}$ , respectively. Actually, from examination of the equilibria;



and



we will find

$$\frac{k_1'}{k_1} = \frac{k_{21}'}{k_{21}} = \frac{(\text{NO}_2')_{\text{equil}}}{(\text{NO})_{\text{equil}} (\text{O})_{\text{equil}}}$$

and

$$\frac{k_{31}'}{k_{31}} = \frac{(\text{NO}_2')_{\text{equil}}}{(\text{NO}_2)_{\text{equil}}} = e^{-\frac{E}{RT}}$$

( $E$  is the energy of excitation of  $\text{NO}_2$ , which corresponds to the average energy of relative motion of  $\text{NO}$  and  $\text{O}$  -  $RT$ , that is, —

$E = D + RT$ , where  $D$  is the energy of dissociation of  $\text{NO}_2$  into  $\text{NO}$  and  $\text{O}$ , equal to  $71.45 \pm 0.50$  Kcal/mole), or, introducing the equilibrium constant

$$K_c = \frac{(\text{NO})_{\text{equil}} (\text{O})_{\text{equil}}}{(\text{NO}_2)_{\text{equil}}}$$

$$\frac{k'_1}{k_1} = \frac{k'_{21}}{k_{21}} = \frac{1}{K_c} e^{-\frac{E}{RT}}$$

Inserting  $k'_1$ ,  $k'_{21}$ , and  $k'_{31}$  in (2), we will obtain

$$I = k e^{-\frac{E}{RT}} \frac{[k_1 + \sum k_{21}(M_i)] \frac{(\text{NO})(\text{O})}{K_c} + \sum k_{31}(M_i)(\text{NO}_2)}{k + k_1 + \sum k_{21}(M_i) + \sum k_{31}(M_i)} h\nu^* \quad (3)$$

Further, introducing the designations

$$\frac{k_1}{k} = \alpha, \quad \frac{k_{21}}{k} \frac{10^6 N}{RT} = \beta_i, \quad \frac{k_{31}}{k} \frac{10^6 N}{RT} = \gamma_i$$

and converting to expression in atmospheres of partial pressures, we write (3) in the following final form:

$$I = \frac{k}{e} e^{-\frac{D}{RT}} \frac{(\alpha + \sum \beta_i P_i) \frac{P_{\text{NO}} P_{\text{O}}}{K_p} + \sum \gamma_i P_i P_{\text{NO}_2}}{1 + \alpha + \sum \beta_i P_i + \sum \gamma_i P_i} \frac{10^6 N}{RT} h\nu^* \quad (4)$$

On the basis of measurements of the intensity of illumination  $I$ , the partial pressure of atomic oxygen  $P_{\text{O}}$  also can be calculated from this formula if all the remaining quantities entering into it are known.

#### EXPERIMENTAL METHOD AND RESULTS

The object of our investigation was an ordinary (hot) flame of carbon monoxide burning at atmospheric pressure in a mixture of  $\text{CO}$  and oxygen, which, according to the qualitative observations of Gaydon, contains particularly large concentrations of oxygen atoms. The burner shown in Fig. 2 was a quartz tube (3)

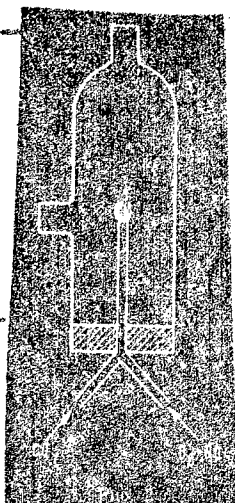


Fig. 2

mm diameter) serving as a nozzle and inserted coaxially into a wide tube (60 mm diameter) of refractory glass. Carbon monoxide and oxygen, contained in separate gasometers, were passed into the nozzle from below, as is shown in Fig. 2. The composition of the mixture, which varied in individual experiments from 33.3% (stoichiometric mixture) to 64.7%  $O_2$ , was regulated by the rate of feed of the gases and was determined by their discharge. Nitric oxide, obtained by the action of dilute nitric acid on copper shavings, was mixed, in quantities of 0.83 to 6.6% of the general pressure, with oxygen on its way to the burner. The experiments consisted of two parts: measurement of the flame temperature; and measurement of the intensity of the yellow-green illumination.

Measurement of the temperature of an oxygen flame of carbon monoxide. In order to measure the flame temperature we used a method of rotation of the D-lines of sodium, introduced into the flame in the form of NaCl. The measurements were carried out in the usual manner, using a standard light source (i.e., a 200 w. projection cinema lamp), two lenses with a focal distance of 8.5 cm, and a direct-vision spectroscope. By using one of the lenses the filament of the lamp was focused on the center of the flame, that is, upon the portion directly located at the top of the inner cone of the flame. The second lens projected the image of the filament and the flame onto the slit of the spectroscope; the diaphragm, which separated the portion of the flame to be investigated, was located between the slit and the flame. The brightness of the filament temperature was measured within limits up to  $2000^\circ C$  by the use of an optical pyrometer of the Gol'bern-Kurl'baum system with a red light filter. The difference in spectral region, upon measurement of the filament temperature (red region,  $\lambda = 655 m\mu$ ) and of the flame colored by sodium (orange region  $\lambda = 589 m\mu$ ), was taken into account by the introduction of the corresponding corrections. The maximum correction for light in our experiments was  $32^\circ$ . Furthermore, a correction of  $10-20^\circ$  was introduced for the dispersion of light in the lenses.

We carried out a series of preliminary experiments on the measurement of flame temperatures of mixtures of air and carbon monoxide of various composition (with CO content from 30 to 89%). The results of these measurements are shown in Fig. 3 (light small circles). As is apparent from the curve in Fig. 3, the temperature of the flame in this case varied within the limits

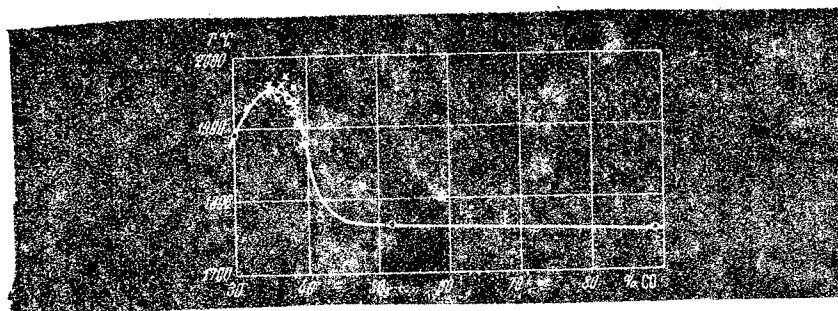


Fig. 3

of 1755 to 1955° C, depending upon the CO content in the mixture, and attained its maximum value at ~35% CO. The measurement data we obtained agree, within the limits of error, with the data of Loomis and Perrot (10), which are also shown in Fig. 3 (cross marks).

The flame temperature of oxygen mixtures of CO, which was the main object of our investigation, considerably exceeded 2000° C, which is the limit of applicability of an optical pyrometer. Therefore, in order to determine the filament temperature of the lamp at incandescence, in this case we had to turn to a method of extrapolation whose applicability is clear from the following reasoning. The amount of thermal energy emitted per unit length of filament is proportional to  $I^2$ , where  $I$  is the current strength furnished to the lamp. However, the quantity of energy lost per unit length of filament, as a result of its small thickness and high temperature, basically should be determined by the illumination whose energy is proportional to  $T^4$ , where  $T$  is the absolute temperature of the filament surface.

Consequently, there results from the thermal balance of the filament a ratio between  $T$  and  $\sqrt{I}$ . This regularity in the region of temperatures from 1000 to 2250° K was confirmed by our special experiments, the results of which are shown in Fig. 4. Here the filament temperature, measured by the use of an optical pyrometer, lies along the ordinate axis; and  $\sqrt{I}$  along the abscissa axis. The temperature of the flame of oxygen mixtures of CO was also determined by the extrapolated portion (dotted line) of the straight line in Fig. 4 according to the value of the incandescent current, which corresponds to the point of intersection of the filament brightness and the D-luminescence of the flame. Temperatures found in this way for flames of mixtures of CO and O<sub>2</sub> of varying composition (from 34 to 80% CO) are shown in Fig. 5. As is apparent from this figure, the maximum temperature was about 2730° K, corresponding to a stoichiometric mixture. We evaluated the error in determination of flame



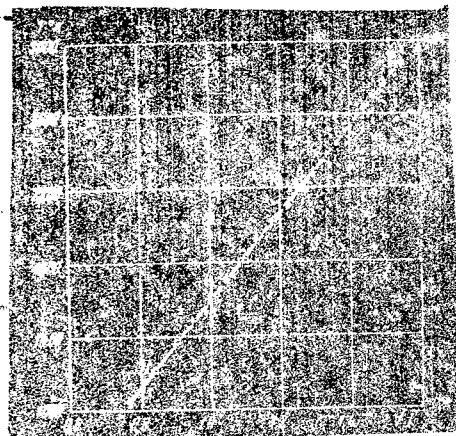


Fig. 4

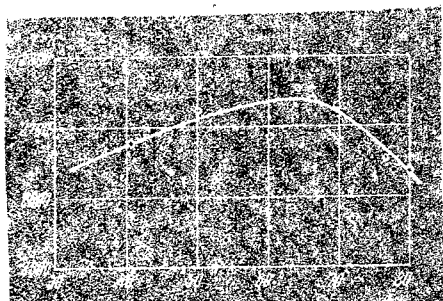


Fig. 5

temperatures of  $\text{CO} + \text{O}_2$  at about  $50^\circ$ , which proved the inaccuracy of visual determination of the moment of rotation of sodium D-lines, as well as the necessity for extrapolation.

We also studied the effect upon the temperature of the flame when nitric acid is added. Measurements were carried out at various compositions of  $\text{CO}$  and  $\text{O}_2$  mixtures by adding  $\text{NO}$  in quantities of 0.6 to 20%. We found that additions of  $\text{NO}$  lower the flame temperature on an average of  $37^\circ$  for every per cent of added nitrogen; and that additions of nitric oxide in quantities greater than 20% extinguish the flame.

Measurement of the absolute intensity of yellow-green emission. The intensity of yellow-green emission was determined spectrophotometrically as the difference in intensity of flame radiation in the presence of nitric oxide and the intensity of illumination occurring on the part of the spectrum of the flame of  $\text{CO}$ . The spectra were photographed using a Pye spectrograph with a glass prism,

having an average dispersion in the region 6500-5500 Å of 90 Å per one millimeter, upon various types of panchromatic photofilm with sensitivity limits up to 7900 Å. The absolute intensities of the flame illumination were determined photometrically by comparison with the intensity of the illumination from a normal Hefner lamp. [authors' footnote: it is known that upon 1 cm of surface placed at a distance of 1 meter, the Hefner lamp emits an energy equal to 900 erg / cm<sup>2</sup> sec. The spectral distribution of the illumination of the Hefner lamp is obtained by the formula:

$$E_\lambda = \text{const.} \lambda^{-6.4} e^{-\frac{1.43}{1750\lambda}}, \lambda \text{ in centimeters.}]$$
 In order to do this, seven spectra were photographed on one film: two spectra of a neon lamp (first and seventh), one  $\text{CO}$  flame spectrum, one spectrum from the same flame but with addition of  $\text{NO}$ , and three spectra of a Hefner lamp with different exposure times serving as standards of intensity. These spectra, further, were photomeasured on a Moll's microphotometer and, by the measured dark areas and the standards of intensity, the relative inter-

Intensity of illumination  $\left(\frac{I}{I_0}\right)_\lambda$  of the flame was determined, corresponding to the definite wave length  $\lambda$  ( $I_0$  is the intensity of illumination of a Haffner lamp) of a neon lamp located along the spectrum. This type of measurement was carried out in the majority of experiments at the following wave lengths: 6507, 6267, 6030, 5764, 5562, and 5400 Å (around 5400 Å is the short-wave length limit of yellow-green emission).

Here it is necessary to mention the following: it was observed that the introduction of NO into a flame of carbon monoxide not only lowers the flame temperature but also decreases its brightness. Therefore, when determining the intensity of yellow-green emission, flame spectra of CO were compared with each other and with the same flame upon the addition of NO; these were made at different exposures selected so that in the short-wave length portion of the spectrum, where there is an absence of superimposed illumination from NO<sub>2</sub> ( $\lambda < 5400$  Å), both spectra gave similar dark areas.

From a determination of the energy in a Haffner lamp spectrum it is not difficult to find the portion of energy occurring at a definite wave length (in the interval  $\Delta\lambda$ ); that is,

$$i_\lambda \Delta\lambda = \frac{E_\lambda \Delta\lambda}{\int_0^\infty E_\lambda d\lambda} = \frac{(I_0)_\lambda \Delta\lambda}{\int_0^\infty (I_0)_\lambda d\lambda},$$

where by multiplying the relative intensities of illumination of a CO flame, obtained by photometric measurements (with and without addition of NO), by  $i_\lambda \Delta\lambda$  ( $I_0)_\lambda d\lambda$  and integrating along the whole spectrum, we will obtain the intensity of illumination of the flame in both cases as

$$\epsilon^{NO} = \int_0^\infty (I_0)_\lambda d\lambda \int_0^\infty \left(\frac{I}{I_0}\right)_\lambda^{NO} i_\lambda d\lambda$$

and

$$\epsilon = \int_0^\infty (I_0)_\lambda d\lambda \int_0^\infty \left(\frac{I}{I_0}\right)_\lambda i_\lambda d\lambda.$$

The difference between these two quantities gives the energy corresponding to yellow-green emission:

$$\Delta\epsilon = \epsilon^{NO} - \epsilon = \int_0^\infty (I_0)_\lambda d\lambda \left[ \int_0^\infty \left(\frac{I}{I_0}\right)_\lambda^{NO} - \left(\frac{I}{I_0}\right)_\lambda \right] i_\lambda d\lambda. \quad (5)$$

Graphically this difference is represented as a square which is included between the curves  $\left(\frac{I}{I_0}\right)_\lambda i_\lambda : \lambda$  for both flames. The

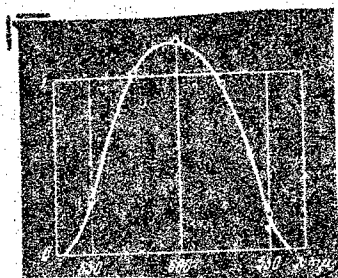


Fig. 6

magnitude of this square is found by graphic integration. In Fig. 6 we introduce the distribution curve for energies in the spectrum of yellow-green emission.

In our experiments the Heffner lamp was located at a distance of  $r_0 = 1$  M from the spectrograph slit, whereas the flame was at a distance of  $r = 0.33$  M. In addition, the times of exposure during photography of the spectrum of the flame ( $t$ ) and the lamp spectrum ( $t_0$ ) were different. Recalculation for similar distances and exposure times gives the following corrected coefficient [authors' footnote: Here as before we assume that darkening of the photofilm is determined by the product of the light intensity and the time of exposure. For photometric measurements which have as their goal evaluation of the order of magnitude of the measured intensities, this rough approach proves quite adequate.]:

$$x = \left( \frac{r}{r_0} \right)^2 \frac{t_0}{t}, \quad (6)$$

which must be multiplied by the quantity  $\Delta \epsilon$  determined by the method described above.

Inserting into the expression  $x \Delta \epsilon$  the value  $\int (I_0)_\lambda d\lambda = 900$  erg/cm<sup>2</sup>sec, we will obtain the energy of the yellow-green emission occurring on one cm of surface which is at a distance  $r$  from the flame. Consequently, in order to determine the full energy of illumination of a unit volume of flame in one second, we obtain in this case

$$I = \frac{4\pi r^2}{v} x \Delta \epsilon \frac{\text{erg}}{\text{cm}^2 \text{cek}} \quad (7)$$

( $v$  is the volume of the flame, equal  $\sim 1$  cm<sup>3</sup>).

Measurements of the quantity  $I$ , using the method described above, were carried out in ten different experiments. The results of these experiments are given in Table 1.

#### DISCUSSION OF THE RESULTS

The quantities  $k, \alpha, \beta_1, \gamma_1, \beta_1$ , and  $v^*$  entering into expression (4) were found from the following data. Investigations of the fluorescence of NO<sub>2</sub> lead to a value of the quantity  $k$  of the order of  $10^5 \text{ sec}^{-1} \text{ cm}^2$  (11). This quantity naturally should not depend upon the excitation energy, that is, upon the wave length. The quantity  $\gamma_1$  was determined by Baxter (12) from the extinguishing of fluorescence of NO<sub>2</sub> by various gases at room

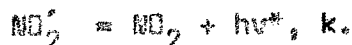
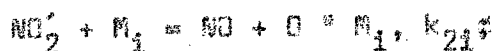
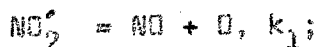
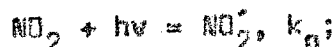
Table 1

| No. of experiments | Mixture composition |      |                | T, °K | I, erg/cm <sup>2</sup> | P, mm | (CO) cal/cm <sup>2</sup> sec | (CO) cal/cm <sup>2</sup> sec |
|--------------------|---------------------|------|----------------|-------|------------------------|-------|------------------------------|------------------------------|
|                    | CO                  | NO   | O <sub>2</sub> |       |                        |       |                              |                              |
| 36                 | 34.6                | 62.8 | 2.6            | 2570  | 78.0                   | 62    | 11                           | 5.6                          |
| 54                 | 40.2                | 46.7 | 4.1            | 2612  | 77.3                   | 17    | 22                           | 1.25                         |
| 55                 | 52.8                | 45.3 | 2.1            | 2557  | 73.0                   | 26    | 35                           | 1.7                          |
| 58                 | 48.1                | 50.3 | 1.6            | 2601  | 76.0                   | 32    | 46                           | 2.25                         |
| 62                 | 40.3                | 47.7 | 1.0            | 2617  | 80.0                   | 17    | 12                           | 2.1                          |
| 64                 | 51.5                | 46.0 | 2.5            | 2593  | 78.3                   | 17    | 13                           | 1.1                          |
| 68                 | 51.3                | 47.9 | 0.8            | 2600  | 77.0                   | 25    | 12                           | 2.1                          |
| 70                 | 63.1                | 34.0 | 2.9            | 2612  | 77.0                   | 14    | 11                           | 2.2                          |
| 71                 | 64.8                | 32.3 | 2.9            | 2603  | 80.0                   | 24    | 8                            | 2.1                          |
| 72                 | 62.2                | 31.5 | 2.3            | 2598  | 76.0                   | 23    | 4                            | 2.25                         |

[legend: (1) no. of experiment; (2) mixture composition; (3) erg/sec; (4) equil ]

temperature and for NO<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> proved equal to 50, 44, 21, and 16.5 mm<sup>-1</sup>, respectively. Since the values of  $\gamma_1$  for effective magnitudes of fluorescence extinguishing which corresponded to these values are close to the gasokinetic magnitude (each gasokinetic collision being extinguishing (11), the quantities also must be considered independent of the wave length. Upon recalculation for the flame temperature T and atm<sup>-1</sup> they must be multiplied by  $760 \sqrt{\frac{300}{T}}$ . In the carbon monoxide flame, gases possessing significant partial pressures are CO<sub>2</sub>, CO, and O<sub>2</sub>. In place of the unknown quantity  $\gamma_{CO}$  we use  $\gamma_{N_2}$ . Further, the quantities  $\alpha$  and  $\beta$  were determined from the data of Holmes and Daniels (8), which refer to the effect of admixtures of foreign gases upon the quantum yield of the photochemical decomposition of NO<sub>2</sub>. In contrast to k and  $\gamma_1$ , these quantities should depend upon wave length, becoming zero when the excitation energy of the molecules becomes less than its dissociation energy D. Holmes and Daniels studied most thoroughly the effect of various amounts of CO<sub>2</sub> upon the quantity  $\eta$ , in which the most accurate of three series of experiments using various wave lengths (40, 366, and 313 m $\mu$ ) were those at  $\lambda = 366$  m $\mu$ . But since the average excitation energy of a molecule of NO<sub>2</sub> under the flame conditions (T = 2500-2700° K) corresponds to  $\lambda \sim 370$  m $\mu$ , then we also use the data for these experiments for the determination of the quantity  $\beta_1$  for CO<sub>2</sub>.

The following processes are the basis of the mechanism of photochemical decomposition of NO<sub>2</sub>:



By using designations taken earlier, we will obtain for the quantum yield at the pressure of an extraneous gas equal to  $p$ ,

$$\eta_p = 2 \frac{\alpha + \beta \text{NO}_2 P_{\text{NO}_2} + \beta p}{1 + \alpha + (\beta \text{NO}_2 + \gamma \text{NO}_2) P_{\text{NO}_2} + (\beta + \gamma) p} \quad (8)$$

Introducing the quantity

$$\eta_0 = 2 \frac{\alpha + \beta \text{NO}_2 P_{\text{NO}_2}}{1 + \alpha + (\beta \text{NO}_2 + \gamma \text{NO}_2) P_{\text{NO}_2}}, \quad (9)$$

that is, the quantum yield at  $p = 0$ , from (8) and (9) we will find

$$\frac{\eta_0}{\eta_0 - \eta_p} = C_1 + \frac{C_2}{p}, \quad (10)$$

where

$$C_1 = \frac{1}{1 - \frac{2}{\eta_0} \frac{\beta}{\beta + \gamma}}$$

and

$$C_2 = \frac{\alpha + \beta \text{NO}_2 P_{\text{NO}_2}}{\beta} \frac{1}{\frac{\eta_0}{2} \frac{\beta + \gamma}{\beta} - 1}$$

The relationship of the quantity  $\frac{\eta_0}{\eta_0 - \eta_p}$  to  $\frac{1}{p}$  according to the data of Holmes and Daniels ( $\lambda = 366 \text{ m}\mu$ ) for  $\text{CO}_2$  is given in Fig. 7, from which it is apparent that this quantity is actually a linear function, in agreement with formula (10). From Fig. 7 we find  $C_1 = 2$  and  $C_2 = 0.8 \cdot 10^3 \text{ mm Hg std.}$  Substituting in the expression for  $C_1$ ,  $\eta_0 = 1.83$  (8), we will obtain  $\frac{\gamma}{\beta} = 1.18$  where it follows that in the region  $\lambda = 366 \text{ m}\mu$ ,  $\beta \approx \gamma$ . Consequently, |

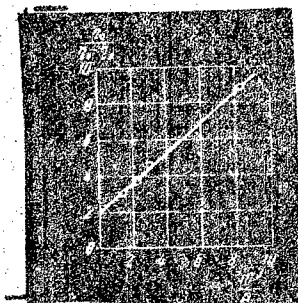


Fig. 7

the excited molecule of  $\text{NO}_2$ , which has an excitation energy corresponding to  $\lambda = 366 \text{ m}\mu$ , is likely to lose its energy of excitation upon collision with a molecule of  $\text{CO}_2$  with the same probability that it will dissociate upon this collision into  $\text{NO}$  and  $\text{O}$ . Taking into consideration the fact that the approximate equilibrium of the quantities  $\beta$  and  $\gamma$  takes place also in the case of other gases, we will set  $\beta_i \approx \gamma_i$ . From here, using the expressions for  $C_2$  and  $\eta_0$  (9), we find  $\alpha \approx 3 \cdot 10^4$ .

Further, calculating the partial pressures of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  in the flame as the average value from the initial and final pressures of these gases (assuming complete combustion of  $\text{CO}$ ) we will have

$$\bar{P}_{\text{CO}_2} = \frac{x}{x+2}, \quad \bar{P}_{\text{CO}} = \frac{1}{2} \frac{x}{x+1} \quad \text{and} \quad \bar{P}_{\text{O}_2} = 1 - \bar{P}_{\text{CO}_2} - \bar{P}_{\text{CO}} \text{ atm.}$$

where  $x = P_{\text{CO}}^0 : P_{\text{O}_2}^0$  is the quantity found from the composition of the initial mixture. These average values of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  also were used during the calculation of the quantity  $\beta_c$  from (4).

Finally, as is apparent from Fig. 6, the maximum emission in the yellow-green spectrum occurs at the wave length  $\lambda^* = 600 \text{ m}\mu$ ; this number also determines the value of the quantity  $v^*$  entering into expression (4).

In expression (4), along with the term which is proportional to the products  $P_{\text{NO}} P_{\text{O}}$ , a term enters which is proportional to

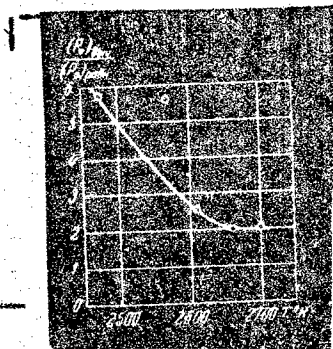
$P_{\text{NO}_2}$ . We will demonstrate that in view of the smallness of the partial pressure of  $\text{NO}_2$  in the flame this second term is insignificantly small in comparison to the first. In order to prove this, it is necessary to demonstrate that  $P_{\text{NO}_2}$  under the conditions in the flame is significantly less than the value  $P_{\text{NO}_2}^{\text{equil}}$  in equilibrium with it. Actually, keeping the relationship of both numerators of (4) we will find

$$\frac{\sum \beta_i P_i P_{\text{NO}}}{(\alpha + \sum \beta_i P_i) P_{\text{NO}} P_{\text{O}}} K_p < \frac{P_{\text{NO}_2}}{(P_{\text{NO}_2}^{\text{equil}})} \frac{(P_{\text{NO}})^{\text{equil}}}{P_{\text{NO}}} \frac{(P_{\text{O}})^{\text{equil}}}{P_{\text{O}}} < \frac{P_{\text{NO}_2}}{(P_{\text{NO}_2})^{\text{equil}}}$$

since  $P_{\text{NO}}$  almost exactly equals  $(P_{\text{NO}})^{\text{equil}}$ , and the partial pressure of oxygen atoms under the conditions of the reaction taking place cannot be less than  $(P_{\text{O}})^{\text{equil}}$ .

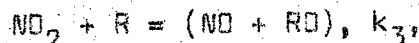
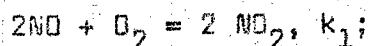
According to data cited in the survey of Geib (13), mole-

Fig. 8



cules of  $\text{NO}_2$  easily react with atoms of  $\text{H}^\cdot$  (the activation energy is less than 5 Kcal). In practice, however, the equilibrium of the double quantum yield, upon photochemical decomposition of  $\text{NO}_2$  in the region of predissociation (Fig. 1), may be viewed as a direct indication of a rapid reaction of  $\text{NO}_2$  also with atoms of  $\text{O}$ . From here it follows that the flame conditions due to the presence of significant concentrations of free atoms and radicals, should be favorable for the decomposition of  $\text{NO}_2$  which also leads to  $P_{\text{NO}_2} \ll (P_{\text{NO}_2})_{\text{equil}}$ .

Considering the reaction of  $\text{NO}_2$  with these active particles and designating their concentrations by  $(R)$ , in a stationary burning flame containing  $\text{NO}$  and  $\text{NO}_2$  we will have the processes:



from which it follows

$$\frac{d(\text{NO}_2)}{dt} = 0 = 2k_1(\text{NO})^2 (\text{O}_2) - 2k_2(\text{NO}_2)^2 - k_3(\text{NO}_2)(\text{R}).$$

Introducing the equilibrium constants

$$K_p = \frac{(P_{\text{NO}})_{\text{equil}} (P_{\text{O}})_{\text{equil}}}{(P_{\text{NO}_2})_{\text{equil}}} \quad \text{and} \quad (K_p)_{\text{O}} = \frac{(P_{\text{O}})_{\text{equil}}^2}{(P_{\text{O}_2})_{\text{equil}}},$$

and assuming that  $(\text{NO}) = (\text{NO})_0$  and  $(\text{O}_2) = (\text{O}_2)_{\text{equil}}$ , we will rewrite the preceding equation in the form  $\xi^2 + 2a\xi = 1$ ,

$$\text{where } \xi = P_{\text{NO}_2} / (P_{\text{NO}_2})_{\text{equil}} \quad \text{and} \quad a = \frac{k_3}{4k_1} \frac{(K_p)_0}{K_p (\text{NO})_0 (\text{O})_{\text{equil}}}$$

In view of the fact that  $(\text{R}) \geq (\text{O})_{\text{equil}}$ , it is apparent that

$$a \geq \frac{k_3}{4k_1} \frac{(K_p)_0}{K_p (\text{NO})_0}.$$

The constant  $k_1$  has the value  $0.8 \cdot 10^{-38} \text{ cm}^6 \text{ sec}^{-1}$  (14). We can calculate the constant  $k_3$  by setting the activation energy  $E_3 \approx 10 \text{ kcal}$  and the steric factor equal to 0.1. Such an estimate gives for  $T = 2500\text{--}2700^\circ \text{ abs}$   $k_3 \approx 1 \cdot 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . Finally, the least value of the quantity  $\frac{(K_p)_0}{K_p(\text{NO})_0}$  under the conditions of our experiments was equal to  $2 \cdot 10^{-12} \text{ cm}^{-3}$ ; from this it follows that:  $2a > 10^5$ , i.e.,  $\xi < 10^{-5}$ .

In Table 1, the composition of a mixture is shown for each experiment (second-fourth columns); the flame temperature (fifth column); the amount of energy occurring for the yellow-green emission, calculated according to formula (5) (sixth column); and the partial pressure of the oxygen atoms in the flame, calculated by formula (4) (seventh column). From a comparison with the equilibrium pressures (eighth column), calculated from the average values of  $P_{\text{O}_2}$  and the equilibrium constant  $(K_p)_0$ , it follows that  $P_{\text{O}}$  and  $(P_{\text{O}})_{\text{equil}}$  have close orders of magnitude.

The values of the ratio  $P_{\text{O}}:(P_{\text{O}})_{\text{equil}}$  (eighth column) as a function of temperature of the flame are graphically shown in Fig. 8, in which the data relating to close temperatures are averaged (experiments 54, 63, 70, and 71--average temperature  $2610^\circ \text{ K}$ ; and experiments 56, 58, and 64--average temperature  $2660^\circ \text{ K}$ ). As is apparent from Fig. 8, all the points except one lie on a smooth curve, which can be given the following interpretation. From the data pertaining to the low-temperature exhausted flames of carbon monoxide (2), it is known that in these flames the concentration of atoms and radicals is a thousand times greater than their equilibrium concentration. Upon increasing the flame temperature, that is, approaching combustion conditions which take place in a hot flame, the difference between the actual and equilibrium concentrations of active particles should constantly decrease. It is possible that this also is reflected in the curve of Fig. 8, from which it is possible to draw conclusions about the agreement of both concentrations at flame temperatures exceeding  $2600^\circ \text{ abs}$ . As far as extraneous points are concerned (experiment 35), the increase of  $P_{\text{O}}$  over  $(P_{\text{O}})_{\text{equil}}$  is relatively great here, possibly because of the great excess of oxygen (see Table 1).

#### CONCLUSIONS

Measurement of the intensity of yellow-green emission of  $\text{NO}_2$  leads to the possibility of quantitative evaluation of the



concentration of atomic oxygen in flames. Consequently, a method proposed by Gaydon as qualitative has been converted into a quantitative method of analysis.

By using this method, measurements of the concentration of oxygen atoms in hot flames of carbon monoxide are of the same order of magnitude as the equilibrium concentration (at flame temperatures higher than 2600° abs).

An inadequacy of the method is the quite definite obstacle — that introduction of nitric oxide into the flames changes the combustion conditions (particularly, it lowers the flame temperature). Correspondingly, the measured concentrations of the oxygen atoms apply to flames burning under changed conditions and not to the initial flame.

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